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PADE AS many sheets as necessary) INFORMATION DISCLOSURE STATEMENT BY APPLICANT

Sheet 1 of 1

Complete if Known	
10/573,117	
March 23, 2006	
Toru Harada et al.	
Unassigned	
1019519-000513	
	10/573,117 March 23, 2006 Toru Harada et al. Unassigned

U.S. PATENT DOCUMENTS					
Examiner Initials	Document Number- Kind Code	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines Where Relevant Passages or Figures Appear	
	US-4,737,190 A	04-12-1988	Shimada, et al.		
	US-6,281,917 B1	08-28-2001	Katsuragi, et al.		
	US-6,238,442 B1	05-29-2001	Schumacher, et al.		
	US-				

FOREIGN PATENT DOCUMENTS											
	Foreign Patent Document			STATUS							
Examiner Initials	Country Code ¹ , Number, Kind Code	Publication Date (MM-DD-YYYY)	Name of Patentee or Applicant of Cited Document	Translation	Partial Translation	Eng. Lang. Summary	Search Report	IPER	Abstract		d in Spec. / g. No(s).
	JP 10-279858	10-20-1998	Mitsubishi Chem Corp.				х		х		
	EP 1 437 388 A1	07-14-2004	Fuji Photo Film Co., Ltd.				х				
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Examiner	Date	
Signature	 Considered	



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European Patent Office

Office européen des brevets



(11) EP 1 437 388 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication: 14.07.2004 Bulletin 2004/29

(51) Int Cl.7: C09B 67/22, C09D 11/00

(21) Application number: 04000276.8

(22) Date of filing: 08.01.2004

(84) Designated Contracting States:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IT LI LU MC NL PT RO SE SI SK TR
Designated Extension States:

AL LT LV MK

(30) Priority: 08.01.2003 JP 2003002408 21.10.2003 JP 2003360370 26.12.2003 JP 2003432210

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(54) Coloring composition and inkjet recording method

(57) The invention provides a water-soluble ink capable of forming an image having good color hue and high fastness in various use and environmental conditions, which comprises a coloring composition comprising a disazo dye represented by the following formula 1: A₁-N=N-A₂-N=N-A₃ and at least one other dye having

a specific structure; in formula 1, A_1 , A_2 and A_3 each independently represents an aromatic group which may be substituted or a heterocyclic group which may be substituted, and A_1 and A_3 each is a monovalent group and A_2 is a divalent group.

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Description

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FIELD OF THE INVENTION

[0001] The present invention relates to a coloring composition (preferably a coloring composition (an ink composition, preferably an inkjet ink composition) for forming a color image) containing a combination of an azo dye mainly using a heterocyclic ring as the raw material with an azo dye or the like having a specific structure, and at least a solvent. The present invention also relates to an inkjet recording method using the coloring composition (preferably, black coloring composition).

BACKGROUND OF THE INVENTION

[0002] The inkjet recording method is abruptly overspread and still making a progress, because the material cost is low, high-speed recording can be performed, noises are less generated at the recording and color recording is facilitated.

[0003] The inkjet recording method includes a continuous system of continuously jetting out a liquid droplet and an on-demand system of jetting out a liquid droplet according to image information signals, and the ejection system therefor includes a system of jetting out a liquid droplet by applying a pressure using a piezoelectric element, a system of jetting out a liquid droplet by generating bubbles in an ink under heat, a system using an ultrasonic wave, and a system of jetting out a liquid droplet by suction using an electrostatic force. With respect to the inkjet recording ink, an aqueous ink, an oily ink or a solid (fusion-type) ink is used.

[0004] The coloring agent used in such an inkjet recording ink is required to exhibit good solubility or dispersibility in a solvent, enable high-density recording, provide good color, be fast to light, heat and active gases in the environment (for example, oxidative gas (e.g., NOx, ozone) and SOx) and highly resistant against water and chemicals, ensure good fixing property and less blurring on an image-receiving material, give an ink having excellent storability, have high purity and no toxicity and be available at a low cost. However, it is very difficult to find out a coloring agent satisfying these requirements in a high level. In particular, a dye having good color hue and being fast to light, humidity and heat, especially at the printing on an image-receiving material having an ink-accepting layer containing a porous inorganic white pigment particle, being fast to oxidative gases in the environment, such as ozone, is strongly demanded.

[0005] As the dye for black color, a mixture of a disazo or trisazo dye with a yellow or magenta dye has been heretofore developed and for the raw material of these disazo and trisazo dyes, non-heterocyclic compounds such as phenol, naphthol, naphthylamine and aniline are being widely used. As for the disazo dye obtained from such raw materials, the dyes disclosed, for example, in European Patent No. 0761771 and Japanese Patent No. 2716541 are known, however, these dyes all are poor in the light fastness and furthermore, the fastness to oxidative gases such as ozone is extremely insufficient. Therefore, if such a dye is mixed with a yellow or magenta dye, the problem of poor light fastness or very insufficient fastness to oxidative gases such as ozone remains unsolved.

SUMMARY OF THE INVENTION

[0006] The present invention has been made to solve those problems in conventional techniques and achieve the following objects.

[0007] That is, an object of the present invention is to provide an ink composition for printing such as inkjet printing or an aqueous ink composition for writing, which gives a color image or colored material having good black color hue and excellent fastness.

[0008] Another object of the present invention is to provide an ink composition for inkjet recording and an inkjet recording method, which can form an image having good black color hue and high fastness to light and active gases in the environment, particularly ozone gas.

[0009] As a result of extensive investigations on various dye compound derivatives to obtain a dye ensuring good color hue and high fastness to light and ozone, the present inventors have found that the above-described objects of the present invention can be attained by mixing an azo dye mainly using a heterocyclic ring as the raw material with an azo dye having a specific structure and/or a metal phthalocyanine dye.

1. A coloring composition comprising a dye represented by the following formula 1 and at least one dye selected from the dyes represented by the following formulae 2 to 6:

Formula 1:

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A1-N=N-A2-N=N-A3

Formula 2:

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$$B_1 - N = N - B_2 - N - C - N - D_1$$

Formula 3:

$$E_1 - N = N - E_2 - \frac{H}{N} \qquad N - F_1$$

Formula 4:

Formula 5:

$$J_1 - N = N$$

$$R_5 - N$$

$$N$$

$$R_4$$

Formula 6:

$$L_1 - N = N \xrightarrow{M_2 = M_1} N \xrightarrow{R_6} R_7$$

wherein in formula 1, A_1 , A_2 and A_3 each independently represents an aromatic group which may be substituted, or a heterocyclic group which may be substituted, and A_1 and A_3 each is a monovalent group and A_2 is a divalent group;

in formula 2, B₁ and B₂ each independently represents an aromatic group which may be substituted, or a heterocyclic group which may be substituted, and D₁ represents an arbitrary substituent;

in formula 3, E1 and E2 each independently represents an aromatic group which may be substituted or a hetero-

cyclic group which may be substituted, E_1 is a monovalent group and E_2 is a divalent group, F_1 represents an arbitrary substituent, and R_1 represents a monovalent group;

in formula 4, G₁ and G₂ each independently represents an aromatic group which may be substituted, or a heterocyclic group which may be substituted, and R₂ represents an arbitrary substituent except for hydrogen;

in formula 5, R_3 and R_5 each independently represents a hydrogen atom, an alkyl group, a cycloalkyl group, an aralkyl group, an alkyl group or an aryl group, R_4 represents a hydrogen atom, an alkyl group, a cycloalkyl group, an aralkyl group, a carbamoyl group, an acyl group, an aryl group or a heterocyclic group, and J_1 represents an aromatic group which may be substituted, or a heterocyclic group which may be substituted; and

in formula 6, L_1 represents an aromatic group which may be substituted, or a heterocyclic group which may be substituted; M_1 and M_2 each represents = CR_8 - or - CR_9 =, or either one of M_1 and M_2 represents a nitrogen atom and the other represents = CR_8 - or - CR_9 =; R_6 and R_7 each independently represents a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, an alkylsulfonyl group, an arylsulfonyl group or a sulfamoyl group, and each group may further have a substituent; Q_1 , R_8 and R_9 each independently represents a hydrogen atom, a halogen atom, an aliphatic group, an aromatic group, a heterocyclic group, a cyano group, a carboxyl group, a carbamoyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a heterocyclic oxycarbonyl group, an acyl group, a hydroxy group, an alkoxy group, an aryloxy group, an aryloxycarbonyloxy group, an alkoxycarbonyloxy group, an aryloxycarbonyloxy group, an aryloxycarbonyloxy group, an aryloxycarbonylamino group, an arylo

- 2. The coloring composition as described in the item 1, wherein A_3 in formula 1 represents an aromatic heterocyclic group.
- 3. The coloring composition as described in the item 1 or 2, wherein at least one of A_1 and A_2 in formula 1 represents an aromatic heterocyclic group.
- 4. The coloring composition as described in any one of the items 1 to 3, wherein A_3 in formula 1 represents an aromatic nitrogen-containing 6-membered heterocyclic group.
- 5. The coloring composition as described in any one of the items 1 to 4, wherein the dye represented by formula 1 is a dye represented by the following formula 7:

Formula 7:

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$$A_1 - N = N - A_2 - N = N$$
 V_1
 $T_2 = T_1$
 N
 R_{10}
 R_{11}

wherein T₁ and T₂ each represents = CR₁₂- or -CR₁₃=, or either one of T₁ and T₂ represents a nitrogen atom and the other represents = CR₁₂- or -CR₁₃=; V₁, R₁₂ and R₁₃ each independently represents a hydrogen atom, a halogen atom, an aliphatic group, an aromatic group, a heterocyclic group, a cyano group, a carboxyl group, a carbamoyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a heterocyclic oxycarbonyl group, an acyloxy group, an acyloxy group, an aryloxy group, an aryloxy group, an aryloxy group, an aryloxycarbonyloxy group, an amino group (including an alkylamino group, an alkoxycarbonylamino group, an alkoxycarbonylamino group, an alkylsulfonylamino group, an alkylsulfonylamino group, an alkylsulfonylamino

group, an arylsulfonylamino group, a heterocyclic sulfonylamino group, a nitro group, an alkylthio group, an arylthio group, a heterocyclic thio group, an alkylsulfonyl group, an arylsulfonyl group, a heterocyclic sulfonyl group, an arylsulfonyl group, a sulfamoyl group or a sulfo group, and each group may be further substituted; R_{10} and R_{11} each independently represents a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, an alkylsulfonyl group, an arylsulfonyl group or a sulfamoyl group, and each group may further have a substituent, provided that R_{10} and R_{11} do not represent a hydrogen atom at the same time; and R_{12} and R_{10} , or R_{10} and R_{11} may combine to form a 5- or 6-membered ring.

6. The coloring composition as described in the item 5, wherein the dye represented by formula 7 is a dye represented by the following formula 8 or formula 8-2:

Formula 8:

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$$R_{14}$$
 R_{15}
 R_{10}
 R_{10}
 R_{10}
 R_{11}

Formula 8-2:

wherein R_{14} and R_{15} each has the same meaning as R_{12} of formula 7 and A_1 , R_{10} , R_{11} , T_1 , T_2 and V_1 have the same meanings as in formula 7.

7 The coloring composition as described in any one of the items 1 to 6, wherein the dye represented by formula 2 is a dye represented by the following formula 9:

Formula 9:

$$B_1 - N = N - B_2 - N - C - N - B_3 - N = N - B_4$$

wherein B₁, B₂, B₃ and B₄ each independently represents an aromatic group which may be substituted, or a heterocyclic group which may be substituted.

8. The coloring composition as described in any one of the items 1 to 7, wherein the dye represented by formula 3 is a dye represented by the following formula 10:

Formula 10:

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$$E_1 - N = N - E_2 - \frac{H}{N} \qquad N = N - E_3 - N = N - E_4$$

wherein E_1 , E_2 , E_3 and E_4 each independently represents an aromatic group which may be substituted, or a heterocyclic group which may be substituted, and R_1 represents a monovalent substituent.

9. The coloring composition as described in any one of the items 1 to 8, wherein the dye represented by formula 6 is a dye represented by the following formula 11:

Formula 11:

$$L_{1}-N=N \xrightarrow{R_{13}} N \xrightarrow{R_{12}} N \xrightarrow{R_{6}} R_{7}$$

$$R_{15}-N \xrightarrow{R_{14}} R_{14}$$

wherein L_1 , R_6 and R_7 have the same meanings as in formula 6, R_{12} and R_{13} have the same meanings as R_8 and R_9 , respectively, R_{14} and R_{15} each independently represents a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, a sulfonyl group or a sulfamoyl group.

- 10. The coloring composition as described in any one of the items 1 to 9, which further comprises a metal phthalocyanine dye.
- 11. The coloring composition as described in the item 10, wherein the metal phthalocyanine dye is a dye represented by the following formula 12: